

## Supporting Information

### Selective Dimerization of Ethylene to 1-Butene with a Porous Catalyst

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**General Remarks.**

Nickel nitrate hydrate (99.9%, Strem), methylaluminoxane (10 wt. % in toluene, Sigma), modified methylaluminoxane (MMAO-12, 7 wt. % Al in toluene, Sigma), diethylaluminum chloride (25 wt. % in toluene, Sigma), triethylaluminum (25 wt. % in toluene, Sigma), 1-pentene (analytical standard, 99.5%, Sigma), and ethylene (99.9%, Airgas) were used as received. Dry, deaerated toluene (HPLC Grade, 99.8%) was obtained by passing the solution through two silica columns in a Glass Contour Solvent System and degassing with a flow of argon gas for 30 min followed by three freeze-pump-thaw cycles.

Nickel and zinc analyses (ICP-OES) for Ni-MFU-4l samples were performed by Robertson Microlit Laboratories, Ledgewood, New Jersey. Nickel and iron analyses were conducted at the MIT Center for Environmental Health Sciences (MIT CEHS) using an Agilent 7900 inductively coupled plasma mass spectrometer (ICP-MS). Standards were prepared from solutions purchased from VWR designated suitable for ICP analysis.

Powder X-ray diffraction (PXRD) patterns were recorded on a Bruker Advance II diffractometer equipped with  $\theta/2\theta$  Bragg-Brentano geometry and Ni-filtered Cu-K $\alpha$  radiation ( $K\alpha_1 = 1.5406$  Å). The tube voltage and current were 40 kV and 40 mA, respectively.

A Micromeritics ASAP 2020 Surface Area and Porosity Analyzer was used to measure nitrogen adsorption isotherms. An oven-dried sample tube equipped with a S3 TranSeal™ (Micromeritics) was evacuated and tared. The sample was transferred to the sample tube, heated to 200 °C for 12 h, and held at that temperature until the outgas rate was less than 2 mtorr/minute. The evacuated sample tube was weighed again and the sample mass was determined by subtracting the mass of the previously tared tube. N<sub>2</sub> isotherms were measured using liquid nitrogen baths (77 K). UHP grade (99.999% purity) N<sub>2</sub> and He, oil-free valves and gas regulators were used for all free space corrections and measurements.

The ethylene dimerization reaction mixtures were analyzed with an Agilent 7890B gas chromatograph (30 meter PoraBOND Q PT capillary column) equipped with a 5977A mass spectrometer and a flame ionization detector.

## Experimental details.

MFU-4l was prepared according to the literature.<sup>24,25,26</sup>

**Synthesis of Ni(30%)-MFU-4l.** Ni(NO<sub>3</sub>)<sub>2</sub>•6H<sub>2</sub>O (1.8 g, 6.2 mmol) was dissolved in 15 mL of DMF. MFU-4l (100 mg;  $7.93 \times 10^{-2}$  mmol) was suspended in an additional 5 mL of DMF and added to the Ni(NO<sub>3</sub>)<sub>2</sub>•6H<sub>2</sub>O solution. The resulting suspension was left in an oven heated to 75 °C for 48 hours. The solution was decanted, and the remaining powder was soaked in 20 mL fresh DMF. This process was repeated once daily for three days. The powder was subsequently suspended in 20 mL of fresh methanol. The methanol was replaced once daily for three days. The resulting powder was transferred as a slurry into activation glassware. The material was desolvated at 150 °C under vacuum ( $10^{-5}$  torr) for 18 hours. Number of Ni<sup>2+</sup> ion in the molecular formula: 1.34, as determined by ICP-OES.

**Synthesis of Ni(10%)-MFU-4l.** Ni(NO<sub>3</sub>)<sub>2</sub>•6H<sub>2</sub>O (5.5 g, 19 mmol) was dissolved in 100 mL of DMF. An activated sample of MFU-4l (600 mg, 0.475 mmol) was suspended in an additional 50 mL of DMF and added to the Ni(NO<sub>3</sub>)<sub>2</sub>•6H<sub>2</sub>O solution. The resulting suspension was allowed to sit at room temperature for one month. The solution was decanted, and the remaining powder was soaked in 100 mL fresh DMF. This process was repeated once daily for three days. The powder was subsequently suspended in 100 mL of fresh methanol. The methanol was replaced once daily for three days. The resulting powder was collected via gravity filtration and was transferred into activation glassware. The material was desolvated by heating at 150 °C under vacuum ( $10^{-5}$  torr) for 18 hours. Number of Ni<sup>2+</sup> ion in the molecular formula: 0.46, as determined by ICP-OES.

**Synthesis of Ni(3%)-MFU-4l.** Ni(NO<sub>3</sub>)<sub>2</sub>•6H<sub>2</sub>O (0.5 g, 1.7 mmol) was dissolved in 15 mL of DMF. MFU-4l (100 mg;  $7.93 \times 10^{-2}$  mmol) was suspended in an additional 5 mL of DMF and added to the Ni(NO<sub>3</sub>)<sub>2</sub>•6H<sub>2</sub>O solution. The resulting suspension was left at room temperature for 48 hours. The solution was decanted, and the remaining powder was soaked in 20 mL fresh DMF. This process was repeated once daily for three days. The powder was subsequently suspended in 20 mL of fresh methanol. The methanol was replaced once daily for three days. The resulting powder was transferred as a slurry into activation glassware. The material was

desolvated at 150 °C under vacuum ( $10^{-5}$  torr) for 18 hours. Number of  $\text{Ni}^{2+}$  ion in the molecular formula: 0.17, as determined by ICP-OES.

**Synthesis of Ni(1%)-MFU-4l.**  $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  (0.2 g, 0.4 mmol) was dissolved in 15 mL of DMF. MFU-4l (100 mg;  $7.93 \times 10^{-2}$  mmol) was suspended in an additional 5 mL of DMF and added to the  $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  solution. The resulting suspension was left at room temperature for 24 hours. The solution was decanted, and the remaining powder was soaked in 20 mL fresh DMF. This process was repeated once daily for three days. The powder was subsequently suspended in 20 mL of fresh methanol. The methanol was replaced once daily for three days. The resulting powder was transferred as a slurry into activation glassware. The material was desolvated at 150 °C under vacuum ( $10^{-5}$  torr). Number of  $\text{Ni}^{2+}$  ion in the molecular formula: 0.04, as determined by ICP-OES.

**Synthesis of Ni@(Fe)MIL-101.** The supported catalyst Ni@(Fe)MIL-101 was prepared according to a literature procedure.<sup>16</sup>

**General procedure for ethylene oligomerization.** In a typical catalytic protocol, a magnetic stir bar and desolvated Ni-MFU-4l (5.0 mg,  $4.0 \times 10^{-3}$  mmol) were introduced into a 50-mL stainless steel Parr reactor in a nitrogen filled glovebox. Toluene (5 mL) was added to the reactor, followed by the addition of the specified number of equivalents of MAO. The reactor was sealed, transferred out of the glovebox, and brought to the reaction temperature specified with a temperature controller and internal temperature probe. Thirty minutes after the addition of MAO, the reactor was pressurized with ethylene through a dip tube and magnetic stirring was turned on. After one hour, the reactor was rapidly cooled in a dry ice/acetone bath. When the internal temperature reached  $-20$  °C, the reactor was slowly vented to atmospheric pressure. The reactor was opened and the reaction solution was treated with ice-cold deionized water. Cooled 1-pentene (0.1 mL) was added to the solution to serve as an internal standard before the organic layer was filtered through a precooled 0.2- $\mu\text{m}$  Supor® syringe filter. A small sample of the organic layer was quickly analyzed via gas chromatography. The recovered solids were digested in a 10:1 mixture of methanol and concentrated aqueous HCl to isolate any polymeric products.

Control experiments with the parent all-Zn MFU-4l and with alternative aluminum activators were carried out in an analogous manner as described above.

**Lifetime experiment with Ni-MFU-4l.** We constructed a two-reactor system that allows us to distill the reaction product without exposing the Ni-MFU-4l/MAO slurry to air in order to study the lifetime of Ni-MFU-4l and the potential for catalyst recycling. As with typical oligomerization experiments, a magnetic stir bar and activated Ni-MFU-4l (5.0 mg,  $4.0 \times 10^{-3}$  mmol) were introduced into a 25 mL stainless steel Parr reactor, referred to as reactor 1, in a nitrogen filled glovebox. Toluene (5 mL) was added to the reactor, followed by the addition of 100 equivalents of MAO. The reactor was sealed, transferred out of the glovebox, and the temperature of the reactor was monitored with an internal temperature probe. A 50 mL stainless steel Parr reactor, referred to as reactor 2, was connected to reactor 1 with three feet of 1/8" copper tubing, with the valve connecting reactor 1 to reactor 2 remaining closed. Reactor 2 was evacuated to remove ambient water and oxygen inside the vessel. After evacuation, reactor 2 was cooled below  $-20\text{ }^{\circ}\text{C}$  with a dry ice/acetone bath, and monitored with an internal temperature probe. Thirty minutes after the addition of MAO to Ni-MFU-4l, reactor 1 was pressurized to 50 bar with ethylene through a dip tube and magnetic stirring was turned on. After one hour, reactor 1 was placed in a water bath at room temperature and the connection between reactor 1 and reactor 2 was opened, allowing butenes to condense in the second reactor. After allowing the system to equilibrate for 30 minutes, the connection between reactor 1 and reactor 2 was closed. Reactor 2 was opened, and precooled toluene (10 mL) and 1-pentene (0.1 mL) were added to the vessel. This organic mixture was analyzed via gas chromatography. Reactor 1 was repressurized with ethylene and allowed to react for one hour, while reactor 2 was cleaned and evacuated. This process was repeated over 8 cycles.

**Leaching Experiment with Ni-MFU-4l.** To verify that leached nickel species were not responsible for the observed catalytic activity, a magnetic stir bar and activated Ni-MFU-4l (5.0 mg,  $4.0 \times 10^{-3}$  mmol) were introduced into a 50-mL stainless steel Parr reactor in a nitrogen filled glovebox. Toluene (5 mL) was added to the reactor, followed by the addition of 100 equivalents of MAO. The reactor was sealed, transferred out of the glovebox, and brought to the reaction temperature specified with a temperature controller and internal temperature probe. Thirty minutes after the addition of methylaluminoxane, magnetic stirring was turned on and the

reactor was pressurized with ethylene through a dip tube. After one hour, the reactor was transferred into a nitrogen glove bag and slowly vented to atmospheric pressure. The reactor was opened and the reaction solution was sparged with dry nitrogen for 15 minutes to remove any residual butenes in solution. The solution was subsequently filtered through three 0.2- $\mu$ m Supor® syringe filters and transferred into a second 50-mL stainless steel Parr reactor. This new reactor was sealed, transferred out of the glove bag, and pressurized with ethylene through a dip tube. Internal stirring was maintained throughout the reaction, and after one hour the reactor was rapidly cooled to  $-20\text{ }^{\circ}\text{C}$  with a dry ice/acetone bath. Once the internal temperature reached  $-20\text{ }^{\circ}\text{C}$  the reactor was slowly vented to atmospheric pressure. The reactor was opened and the reaction solution was treated with precooled deionized water. Precooled 1-pentene (0.1 mL) was added to the solution to serve as an internal standard before the organic layer was filtered through a precooled 0.2- $\mu$ m Supor® syringe filter. A small sample of the organic layer was quickly analyzed via gas chromatography.

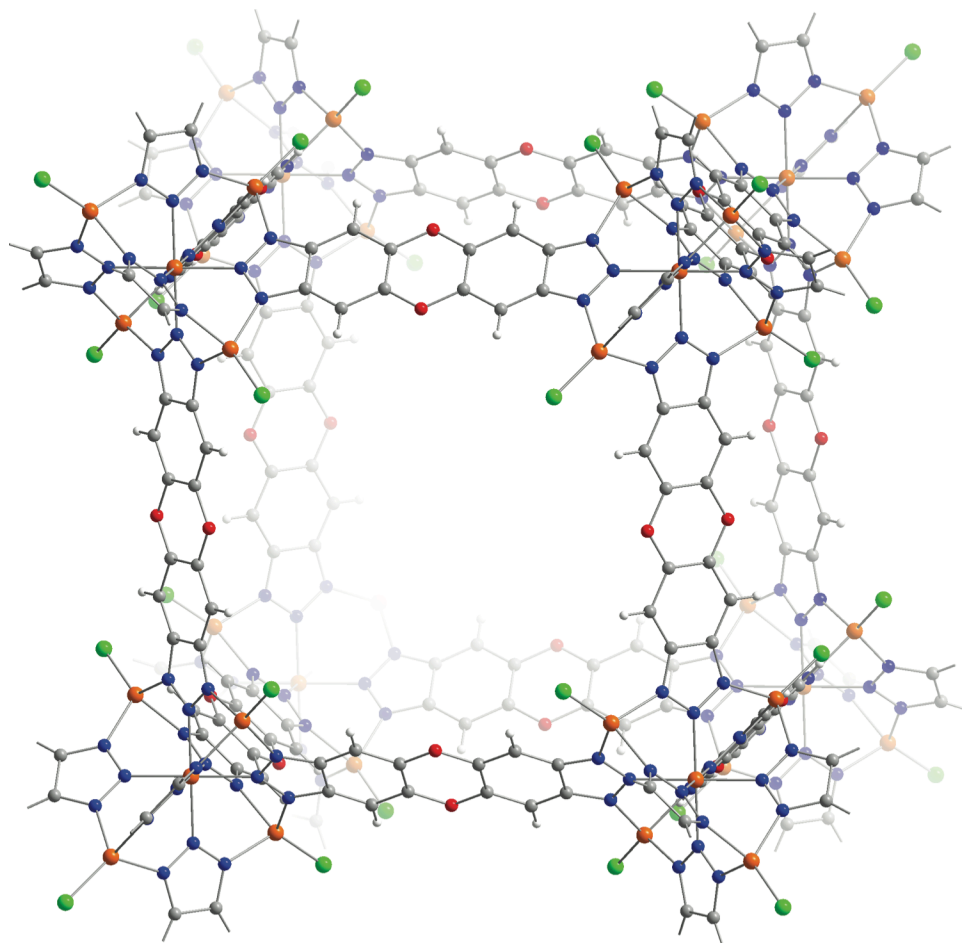
**Ethylene dimerization comparison with Ni@(*Fe*)MIL-101.** To ensure that the increased activity of Ni-MFU-4l relative to other MOF catalysts is not due to reaction conditions, we prepared Ni@(*Fe*)MIL-101 and treated it analogously to Ni-MFU-4l. During the preparation of Ni@(*Fe*)MIL-101, the aluminoxane blend provided by our supplier changed slightly from MAO to MMAO-12, a modified methylaluminoxane activator in which 5% of the methyl groups have been replaced with octyl groups. To ensure that this MAO blend modification does not unfairly bias our comparison between the MOF catalysts, control experiments were performed demonstrating the equivalent catalytic performance of Ni-MFU-4l when activated with either MAO or MMAO-12 (Table S1, entries 1-4). Following these controls, Ni@(*Fe*)MIL-101 was tested under our optimized conditions (Table S1, entry 5), demonstrating the superior performance of Ni-MFU-4l. Furthermore, the PXRD pattern of the recovered Ni@(*Fe*)MIL-101 shows the formation of substantial polymeric deposits (Figure S11).

**Table S1. Comparison between Ni-MFU-4l and Ni@(Fe)MIL-101.**

entry	catalyst	activator	TOF (h <sup>-1</sup> ) <sup>a</sup>	selectivity (wt %)			
				C <sub>4</sub> <sup>b</sup>	C <sub>6</sub> <sup>c</sup>	$\alpha$ -C <sub>4</sub> <sup>d</sup>	Overall 1-butene <sup>e</sup>
1	Ni(1%)-MFU-4l	MAO	41,500	97.4	2.6	94.5	92.0
2	Ni(1%)-MFU-4l	MMAO-12	41,100	97.0	3.0	95.9	93.0
3	Ni(10%)-MFU-4l	MAO	27,000	96.5	3.5	92.3	89.1
4	Ni(10%)-MFU-4l	MMAO-12	26,500	96.1	3.9	91.7	88.1
5	Ni@(Fe)MIL-101	MMAO-12	17,700	89.6	3.6	94.0	84.2

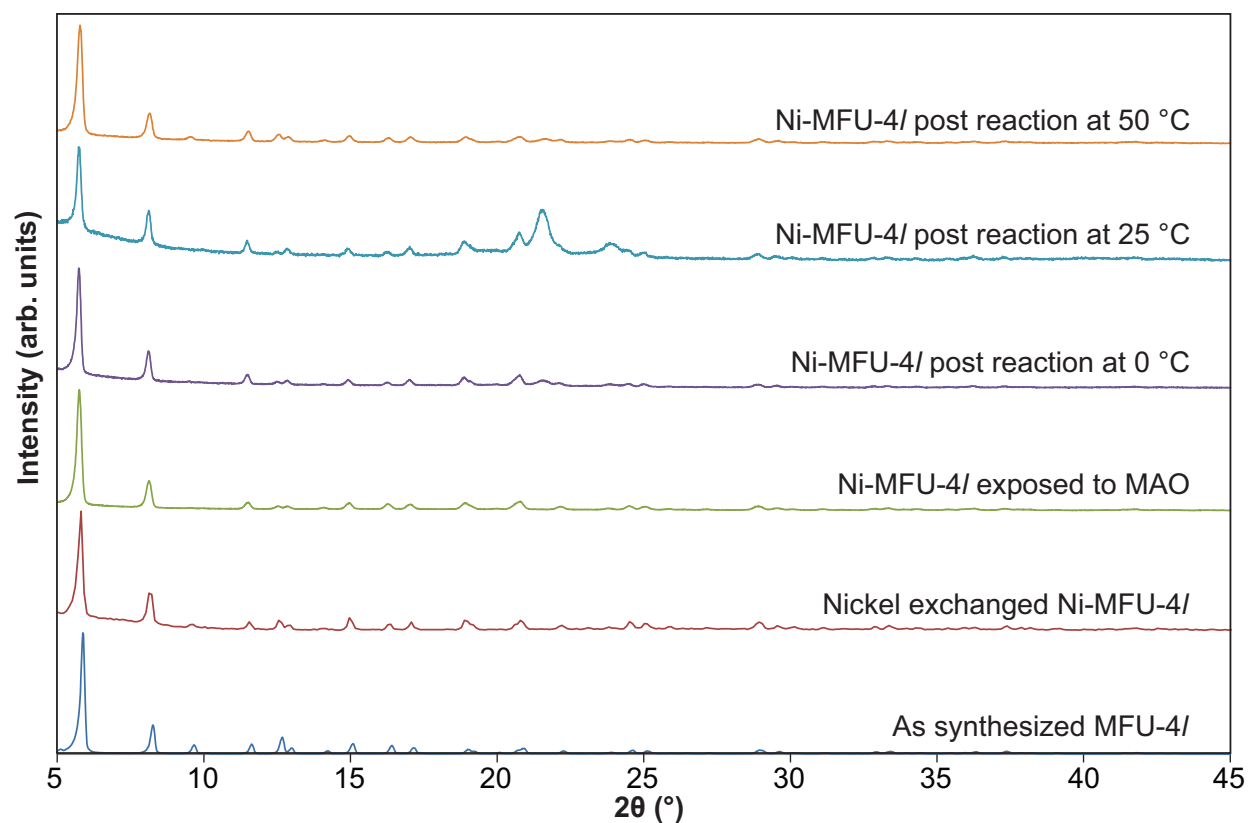
**Table S1.** Comparison of Ni-MFU-4l with Ni@(Fe)MIL-101. All reactions run at 25 °C with 500 equivalents of the alkyl aluminum activator. <sup>a</sup>Moles of ethylene converted per mole of nickel per hour.

<sup>b</sup>The percentage of oligomeric products that are C<sub>4</sub> olefins. <sup>c</sup>The percentage of oligomeric products that are C<sub>6</sub> olefins. <sup>d</sup>The percentage of 1-butene relative to all C<sub>4</sub> products. <sup>e</sup>The overall selectivity for 1-butene among all oligomeric products.

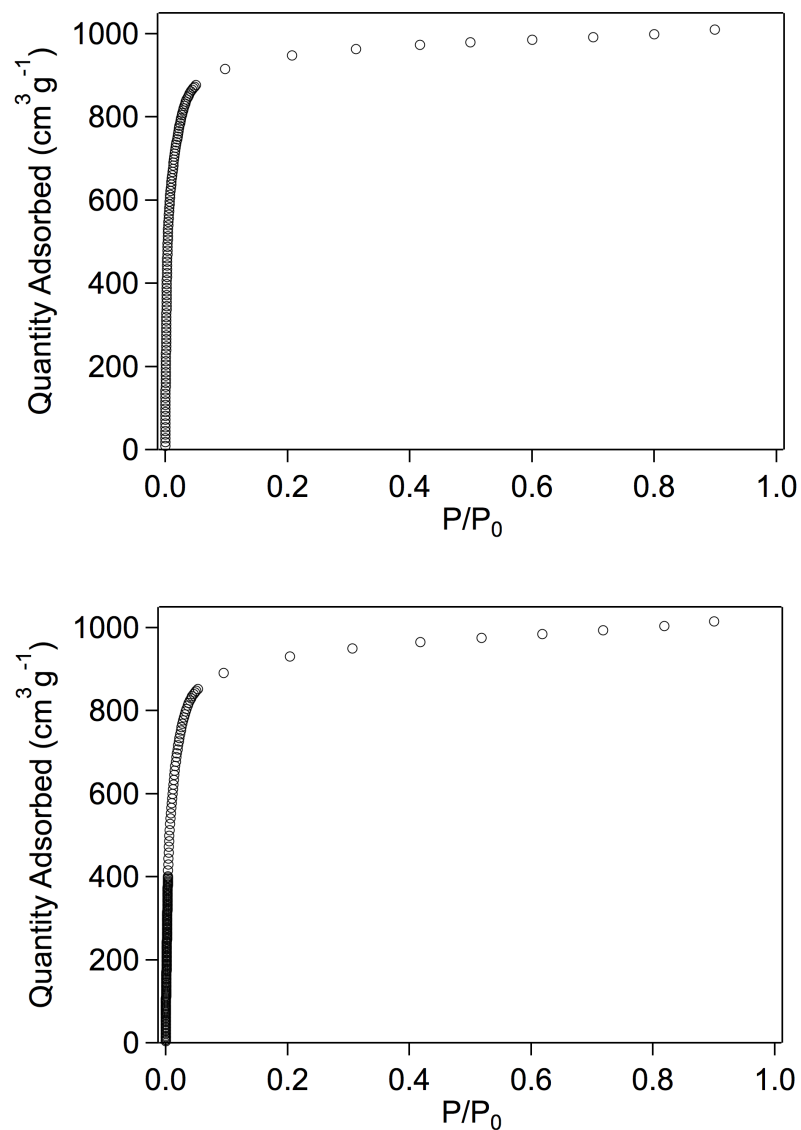


**Figure S1.** A representation of the three-dimensional cubic structure of MFU-4L.

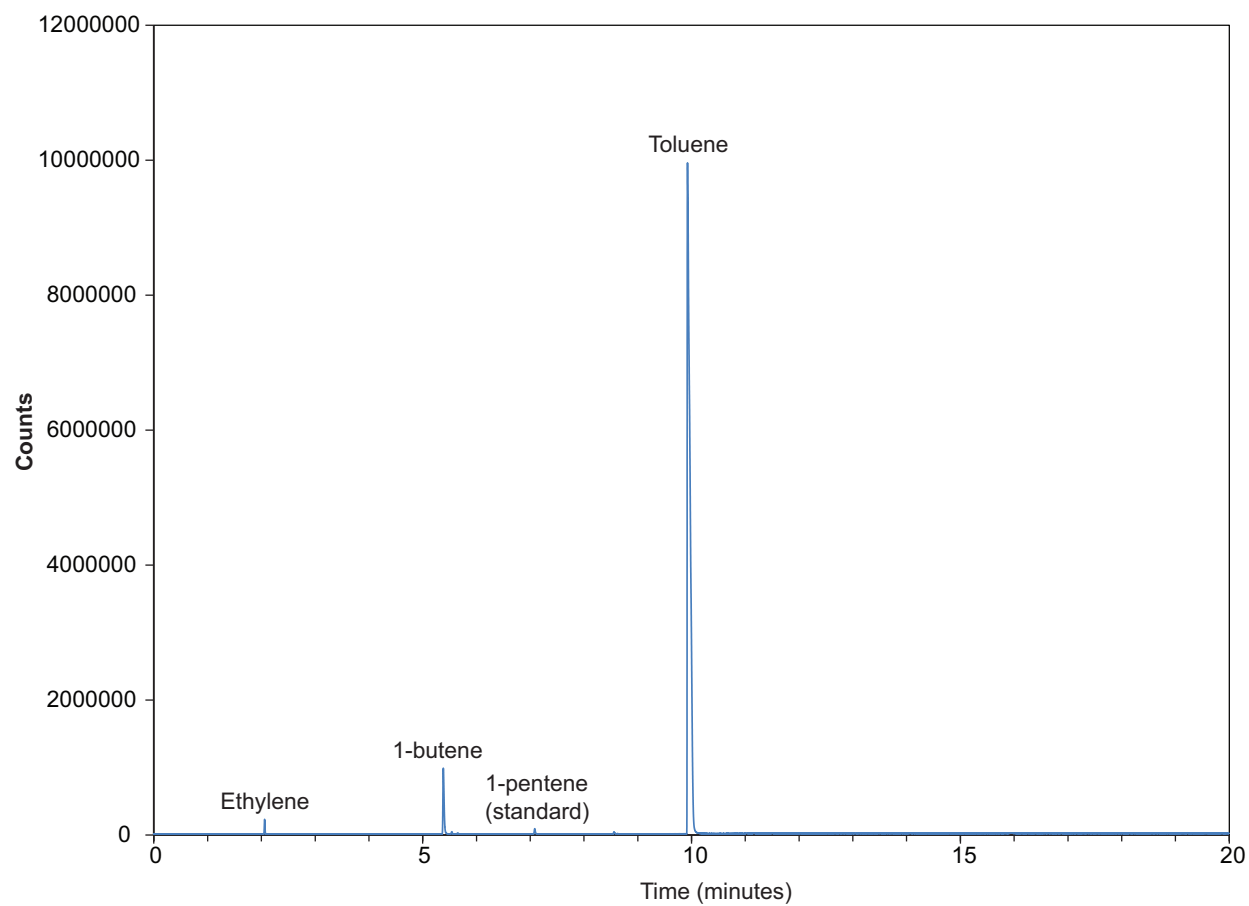




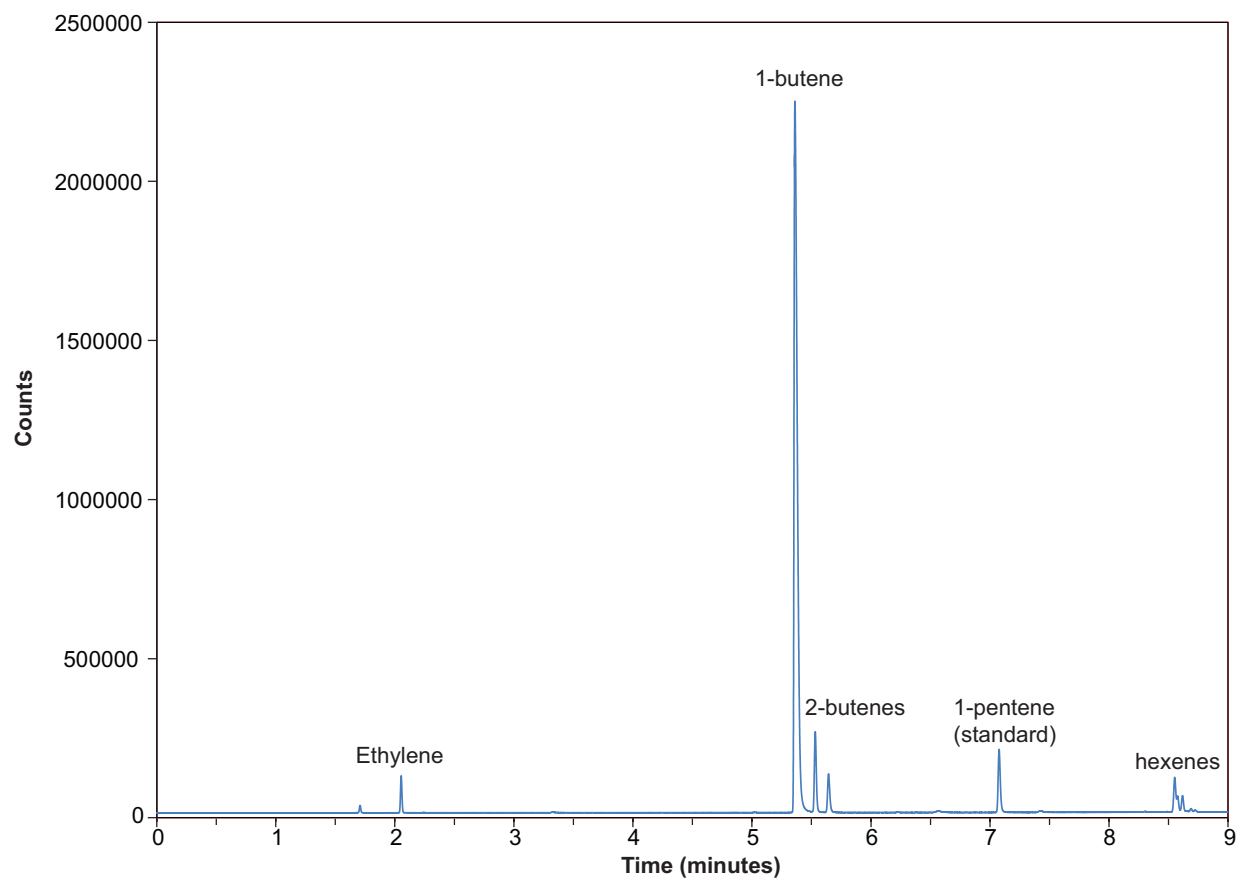
**Figure S2.** PXRD patterns of MFU-4l, Ni-MFU-4l, and Ni-MFU-4l after ethylene oligomerization reactions. The additional peak at 22° observed after reactions performed at 25 °C corresponds to trace polyethylene.



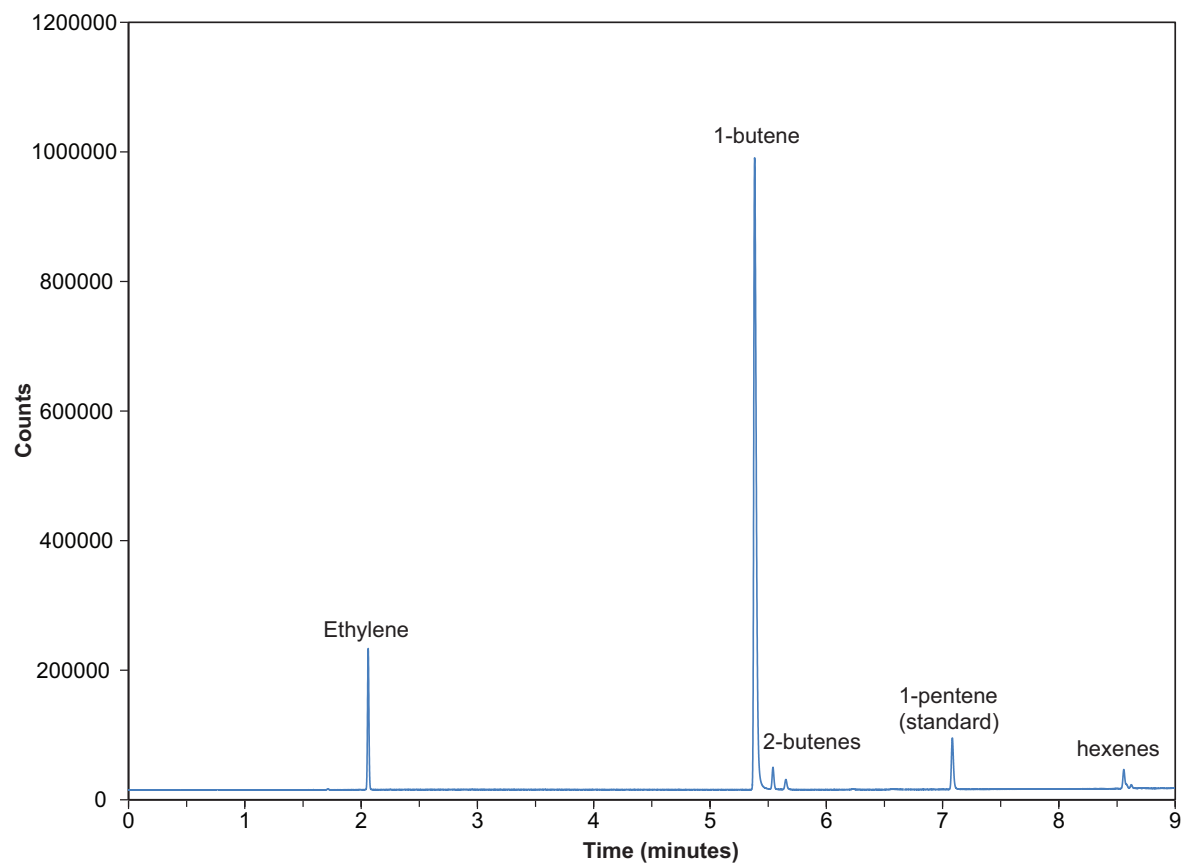
**Figure S3.** Isotherm for the adsorption of N<sub>2</sub> in MFU-4l (top) and Ni(10%)-MFU-4l (bottom) at 77 K. BET analysis of this isotherm gives an apparent surface area of 3,694 m<sup>2</sup>/g for MFU-4l and 3,739 m<sup>2</sup>/g for Ni(10%)-MFU-4l.



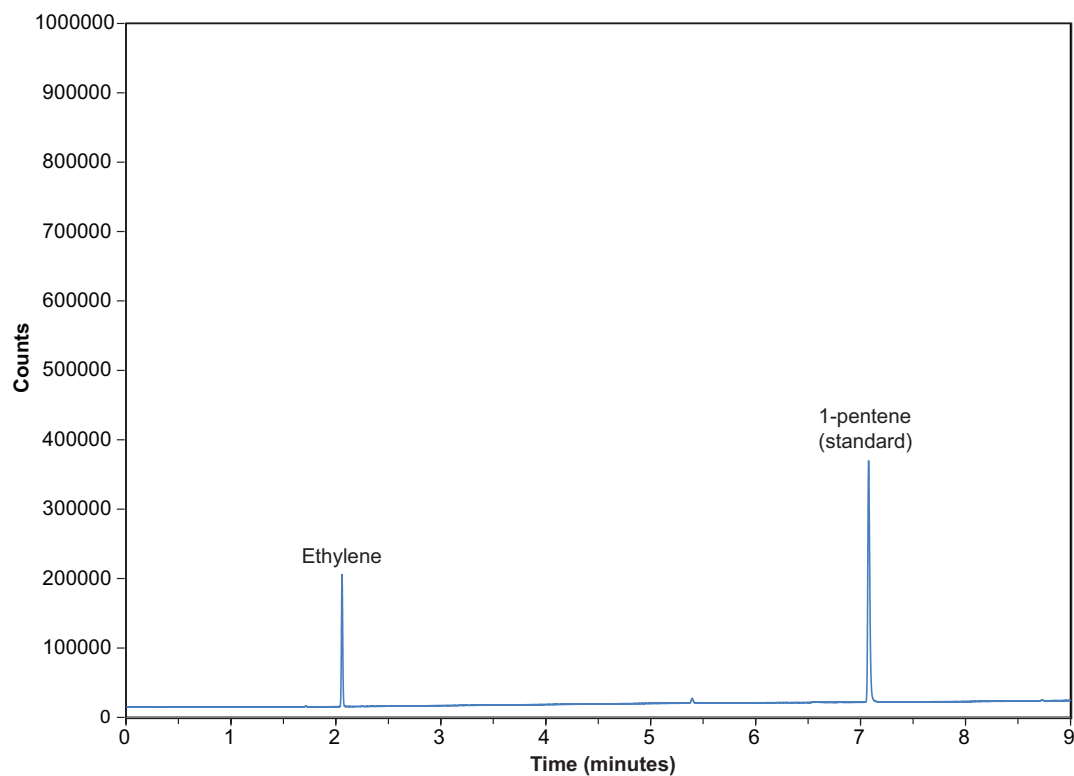
**Figure S4.** Example chromatogram after ethylene dimerization with Ni(10%)-MFU-4l.



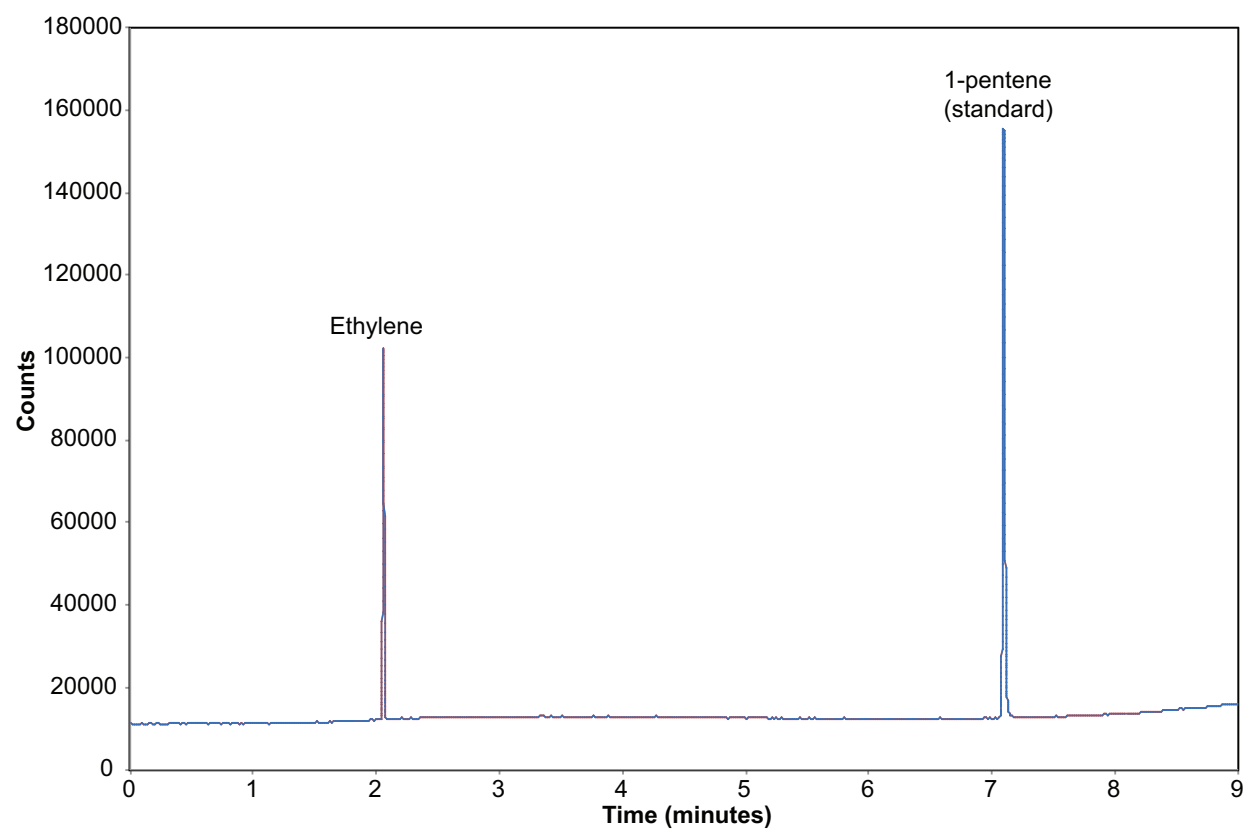
**Figure S5.** Expanded view of product region in the chromatogram in Figure S4.



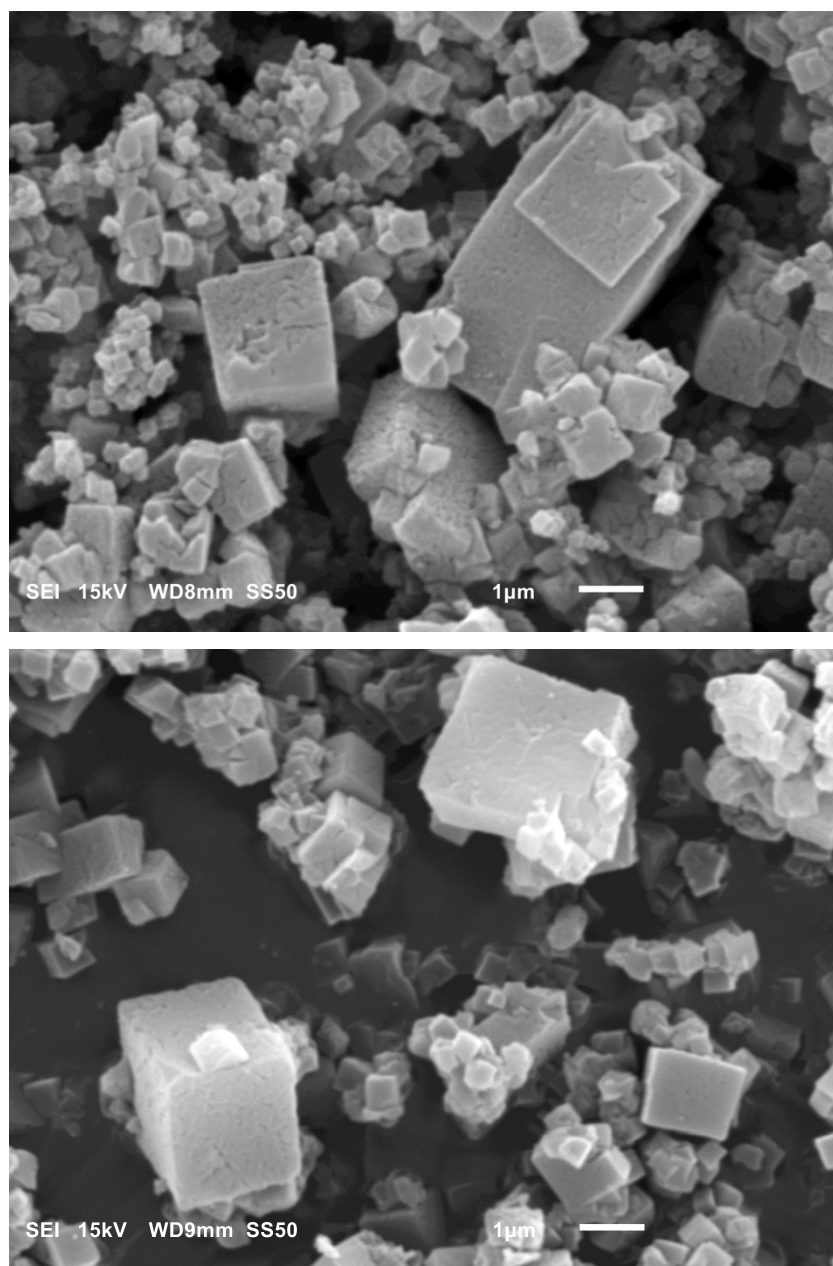
**Figure S6.** Example chromatogram after the most selective conditions for ethylene dimerization with Ni(10%)-MFU-4l.



**Figure S7.** Chromatogram after a control ethylene dimerization experiment with all-zinc MFU-4l and MAO. No detectable product is observed. The control experiment was performed with 5 mg of desolvated MFU-4l under 50 bar of ethylene at 25 °C. An equivalent amount of MAO (as determined by the amount added relative to catalyst mass) was added as in standard ethylene dimerization experiments with Ni-MFU-4l.

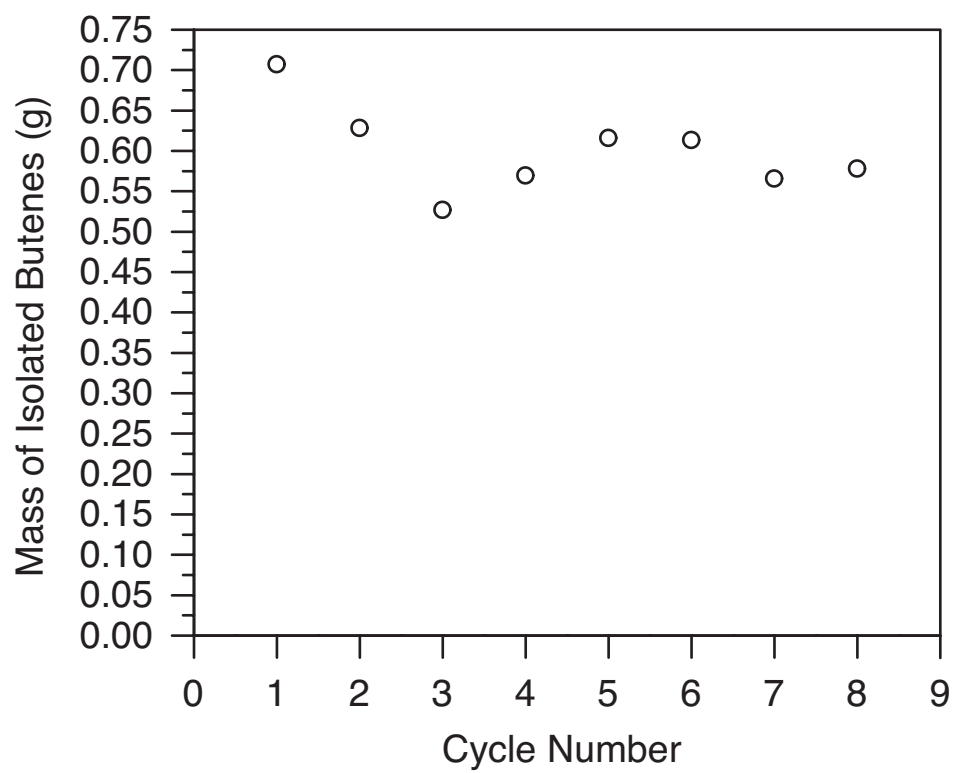


**Figure S8.** GC-FID chromatogram after the leaching experiment. No oligomerization products can be observed.

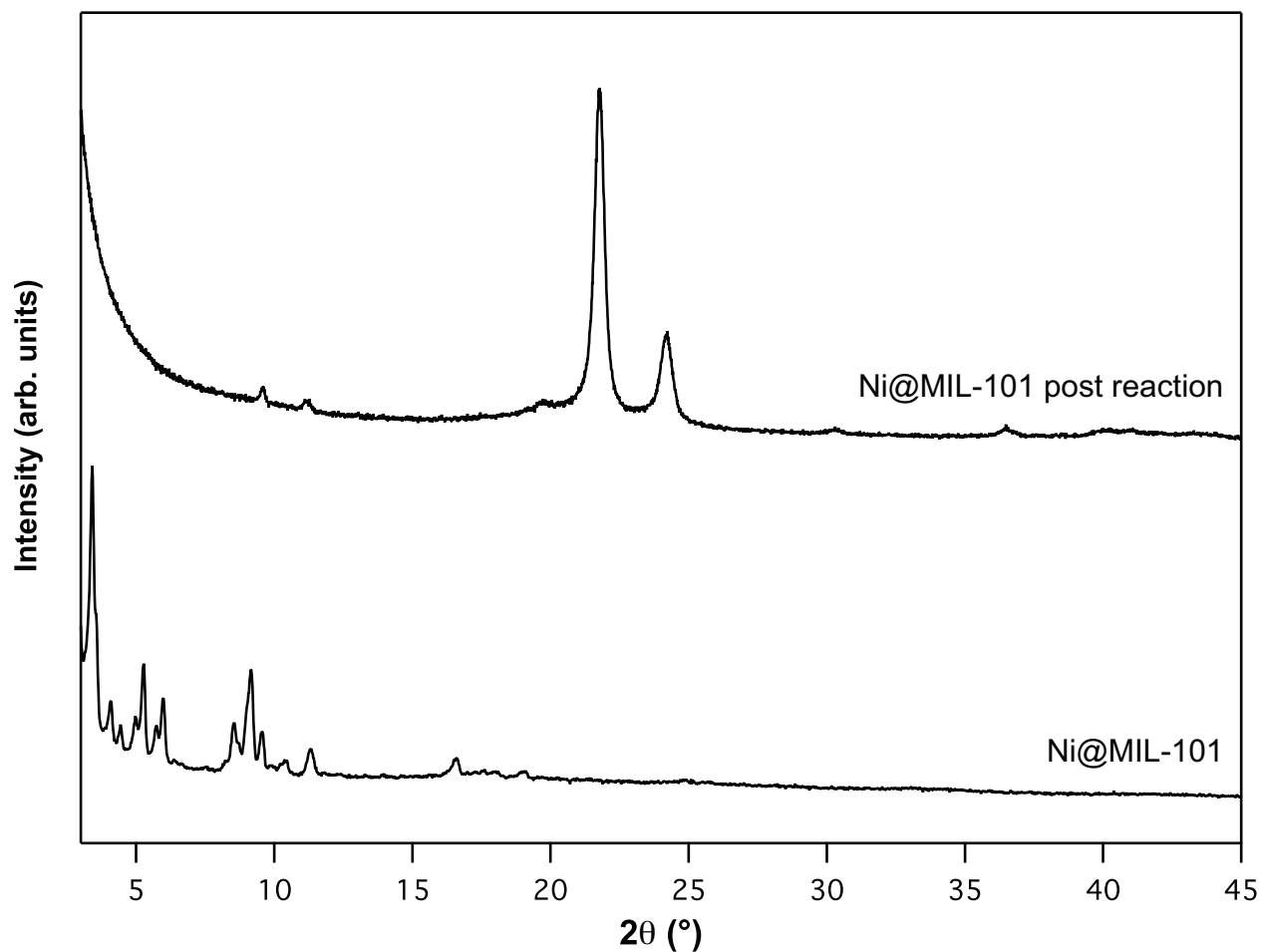


**Figure S9.** Scanning electron micrographs of typical polycrystalline samples of Ni-MFU-4l. The average edge length of a Ni-MFU-4l particle is 0.54 microns.





**Figure S10.** Results of the lifetime experiment with Ni(10%)-MFU-4L.



**Figure S11.** PXRD patterns of Ni@(Fe)MIL-101 before and after an ethylene oligomerization reaction at 25 °C with 500 equivalents of MMAO-12. The PXRD pattern after the reaction is indicative of polyethylene formation.